1 c.c. of water, or 1 part of cobalt in a million parts of water, may be detected readily by the test as now described, this amount giving immediately a claret coloration, and a slight red precipitate on allowing to stand. This method of carrying out the test with the sodium salt is hence far more delicate than the method originally proposed and now in general use; the test may be made even more delicate by using the reagent of one-fifth the concentration recommended above for general use, and comparing the test with a "blank." The colorations obtained with nickel, ferric, etc., salts are all destroyed on acidifying with sulphuric acid. It is immaterial whether the cobalt is present in the solution as nitrate or other salt, provided that it is in the cobaltous condition, whereas Ilinski and Knorre (*loc. cit.*) state that it is necessary to have the cobalt present as chloride or sulphate in order that their method shall succeed.

The test is not affected by the presence of zinc or manganese salts in the solution. The presence of large amounts of nickel interferes with the intensity of the coloration, although it does not prevent the detection of the cobalt, a yellow coloration, and eventually a red precipitate, being obtained with a solution of a sample of nickel ammonium sulphate which contained cobalt, whereas solutions of samples of nickel nitrate and nickel chloride, containing the same concentration of nickel but free from cobalt, gave green solutions on acidifying the test solution with sulphuric acid. For the detection of cobalt in presence of large quantities of nickel, it is advisable to reduce the concentration of the nickel by precipitation with an alcoholic solution of dimethylglyoxime (Tschugaev, *loc. cit.*) or *α*-benzildioxime (Atack, *loc. cit.*). As the presence of either of these nickel reagents in excess gives rise to a cobalt salt which will not react with the nitrosonaphthol reagent, it is essential to separate the nickel partially only.

It is to be noted that this interference with the test by large amounts of nickel is an advantage in general analysis, as the amounts of cobalt present in commercially pure nickel salts do not give a precipitate, but only a coloration, with the new reagent at the concentrations usually employed in qualitative analysis, whereas such amounts are sufficient to give the test with the acetic acid solution in such a manner that, as Chapin remarks (*loc. cit.*), students report cobalt as present in every solution of nickel which they analyse.

The test is not affected by the presence of tartaric or citric acid, which may therefore be employed to keep in solution members of Group III. of the analytical classification; in this manner 0·001 mgrm. of cobalt was readily detected in presence of 1 mgrm. of iron (as ferric ammonium citrate).

The quantitative application of the method is under examination.

Meeting held at the Grand Hotel on Friday, April 9th, 1915.

MR. JULIUS HÜBNER IN THE CHAIR.

THE CONSTANTS OF THE FATTY ACIDS FROM SULPHONATED COD OIL.

BY L. G. RADCLIFFE AND C. W. PALMER.

It is well known that all saponifiable oils can be sulphonated with considerable ease and completeness; moreover, the process is largely carried out on the cheaper oils. A sulphonated oil has properties and constants which differ entirely from the original oil, and it is therefore extremely difficult to identify an oil after it has been sulphonated.

It has been thought useful to sulphonate certain oils and then to hydrolyse the sulphonated product so as to remove completely the sulphonic groups and finally to prepare the fatty acids therefrom and compare their properties with those of the fatty acids from the unsulphonated oil, in the hope that the figures so obtained would prove of use in the analysis and identification of the original oil.

The cod oil used was a brown variety, having a sp. gr. of 0·931 at 15·5° C.; saponification value, 163·3; acid value, 17·6, corresponding to 8·9% of free fatty acid calculated as oleic acid; iodine value, 173·7%.

From this oil the free fatty acids were prepared by saponifying with strong potash and alcohol; the soap was boiled with water to remove the alcohol and the fatty acids precipitated by hydrochloric acid. The clear oil was well washed with water, separated, and heated until free from moisture. The fatty acids had a solidifying point (titer test), 22·8° C.; neutralisation value, 194; mean molecular weight, 289·4; iodine value, 178%; yield of hexabromides, 42%. The sulphonation was performed on 100 grms. of the oil in a suitable vessel cooled with a water-jacket and provided with a thermometer and a mechanical agitator driven by a hot air motor. To the oil 35 grms. of concentrated sulphuric acid was added drop by drop from a tap funnel and the reaction was carefully controlled so that the temperature did not at any time rise above 25° C.; no production of sulphur dioxide was noticed. After two hours stirring no further action was observed, and the darkened and thickened product was washed with a cold saturated solution of sodium sulphate until nearly all the free sulphuric acid was removed. The product dissolved in dilute ammonia to a clear solution. On heating the sulphonated oil in the water-oven a clear oil was obtained, and from this the fatty acids were prepared.

The sulphonated oil was saponified with aqueous caustic potash and alcohol in the same way as was the original oil, and after saponification the fatty acids were liberated as before, well washed, and dried in the water oven. The clear oily fatty acids were tested for sulphur with negative results. These acids were of much harder consistency than the acids from the unsulphonated oil and on examination gave the following data: Solidifying point (titer test), 25·7° C.; neutralisation value, 183; mean molecular weight, 308·6; iodine value, 114·4%; yield of hexabromides, 11·0%. These figures indicate a very extensive alteration in the chemical constitution of the fatty acids regenerated from the sulphonated oil as compared with those of the original cod oil.

The behaviour of other oils is being investigated and the further results will be communicated in a later paper.

DISCUSSION.

MR. J. ALLAN said that the so-called commercial cod oils were mixtures of oils obtained from all kinds of fish, and usually of a dark brown colour, and in an advanced state of decomposition. Such oils were obtained not only from the liver of the fish but also from the entrails. Hence their characteristics were extremely variable. It was, therefore, difficult to understand how the authors could hope to find any means of establishing the origin of sulphonated oils which were of such diverse origin. The treatment of fatty glycerides with sulphuric acid inevitably resulted in the formation of hydroxy acids or stearolactones; the determination of the acetyl value of the oil before and after sulphonation, thus measuring the extent of the introduction of hydroxyl groups into the molecules of the fatty acids, would, therefore, be likely to throw further light on the changes taking place on treating the oil with sulphuric acid.

Mr. L. E. VLIES thought that 8·9 % of free acids was high and that the authors must have been working with "coast cod oil." In his experience maximum sulphonation would not be obtained with ordinary sulphuric acid under the conditions indicated; a longer action and the use of monohydrate being necessary. The power of the sulphonated product to emulsify mineral oil was a useful guide as to the progress of the sulphonation. The sulphonated, or more correctly sulphated, oil was easily hydrolysed by boiling with dilute mineral acid. He asked the authors if they had definitely established that the products of hydrolysis were hydroxylated compounds.

The CHAIRMAN asked whether it could be ascertained what kind of oil or what mixture of oils had been used in the manufacture of a Turkey-red oil. He noted that the fatty acid was different when recovered from the sulphonated oil. That seemed to be borne out by the fact that in dyeing, different shades were produced with different oils.

Mr. F. H. TERLESKI said that coast cod oil sometimes contained 50 % of hydrocarbons. Mr. Vlies had stated that 8 % of free fatty acids was rather high, but it was quite common to get as high a figure as 80 % on the saponifiable matter.

Mr. RADCLIFFE said that he had carried out a considerable amount of research with regard to the acetylation value, and hoped to be able to communicate the results later. The present work had not been carried out with a view to identifying particular cod oils, so that it was immaterial for his purpose whether the oil was adulterated. In reply to Mr. Vlies, the sulphonic group could be eliminated partly by steam and completely by using dilute sulphuric or hydrochloric acid. So far as he had been able to observe, the products appeared to be hydroxyl compounds. He did not know of any method which would identify the original oils in a sulphonated mixture of oils.

THE METAL CONTENT OF SOME LINOLEATES AND ROSINATES.

BY L. G. RADCLIFFE AND C. W. PALMER.

A number of so-called rosinates and linoleates are now offered for various purposes in connection with paints and varnishes, and these are usually made either by fusing an oxide of the metal with rosin, or by saponifying rosin with caustic soda or sodium carbonate, care being taken to avoid an excess of alkali, and then adding a solution of a metallic salt, generally the sulphate or the chloride. The precipitated rosinate, resinate, or sylvinate, as it is variously called, is then washed with water, pressed, and dried.

The precipitated rosinates contain varying percentages of water, whilst those produced by the fusion method are anhydrous. Common rosin or colophony consists almost entirely of abietic acid, and although the metallic salts of this acid are much used in the lacquer and varnish industry as driers and to make substitutes for hard resins, little definite information has been published in regard to their chemical composition. Abietic acid, according to Maly, exists in rosin as the anhydride, but this view is discredited by the ease with which rosin in alcoholic solution can be titrated with alkalis. Mach has isolated a form of abietic acid by extracting rosin with 70 % alcohol and then repeatedly recrystallising the product from 90 % alcohol. The acid which he obtained was white, but melted indefinitely from 148° to 154° C.; he suggested for it the formula, $C_{19}H_{28}O_2$, and this was supported by Tschirch and Studer (Arch. Pharm., 1903, 241, 495). Fahrion obtained a similar acid from American rosin and called it sylvic acid. Various investigators have studied this acid obtained from rosin and have given various formulæ and melting points for it, but the work of Bischoff and Nastvogel, now generally accepted, appears to settle the formula as $C_{20}H_{30}O_2$. It is not necessary to discuss the work of Vesterberg, Haller, Jean, and others on pimaric acid.

Certain salts of abietic acid, described later, have been prepared in connection with a study of the relative efficiency of driers, and we are indebted to Dr. Knecht for a quantity of crystalline abietic acid prepared from French rosin. This acid melted between 149° and 156° C., and had a molecular weight of 304, corresponding to an acid $C_{20}H_{30}O_2$. Since abietic acid is monobasic, as shown by the presence of only one carboxyl group and the proportion of alkali required for its neutralisation, the composition of its metallic compounds can be represented by the formula $(C_{19}H_{29}.COO)_2 : M$, where M represents a divalent metal.

The salts with cobalt, lead, and manganese were prepared by dissolving the abietic acid in alcohol, carefully neutralising with an alcoholic solution of caustic potash, and evaporating the mixture to dryness; the potassium salt was dissolved in water and a solution of cobalt chloride, or manganese chloride, or lead acetate, added until no further precipitate was formed. The precipitate in the case of cobalt was dark heliotrope in colour, the manganese salt faint pink, and the lead salt white. The precipitates were filtered and thoroughly washed with cold water, dried on a porous tile, and then in a water oven until of constant weight.

The cobalt salt was analysed by igniting until free from carbon and then reducing the residual oxide in dry hydrogen and weighing as metal. Calculated for $(C_{20}H_{29}O_2) : Co$, the percentage of cobalt is 8·98; found 9·08 % Co.

The manganese salt was ignited and the residue determined as Mn_3O_4. Calculated for $(C_{20}H_{29}O_2) : Mn$, the percentage of manganese is 8·3; found 8·5 %.

The lead salt was ignited, the residue treated with strong nitric acid, then with strong sulphuric acid, and then weighed as lead sulphate. Calculated for $(C_{20}H_{29}O_2) : Pb$, the percentage of lead is 25·6; found 25·9 %.

The linoleates are prepared from linseed oil by converting it into a soap and then adding a solution of the salt of the metal. It seems rational that such substances should be valued according to the content of metal and also that the loss, presumably of water, at 100°—104° C., should be determined, in the case of the precipitated rosinates; therefore a number of commercial rosinates and linoleates have been examined and the results are recorded herewith.

It may be of interest to describe briefly the different salts and some of the uses for which they have been suggested. Precipitated rosinate of zinc is a fine white powder, and the fused form is in rosin-like lumps. Both are used to harden ordinary rosin; the two are melted together at 180°—190° C., and the product is used to make a cheap varnish. Precipitated rosinate of calcium is a white powder and the fused form is in lumps, as is always the case with the products made by the fusion method. It is used with rosin and linseed oil, giving a product which, when thinned with turpentine, is a form of resin lacquer.

Rosinate of copper has only been examined in the precipitated form; it is a fine green powder used for preparing anti-fouling marine paints and also for wood impregnation.